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<u>L4</u>	((11) AND (L2 SAME L3))	7	<u>L4</u>
<u>L3</u>	monomer	134124	<u>L3</u>
<u>L2</u>	binder OR matrix OR thermoplastic	435059	<u>L2</u>
<u>L1</u>	heterogeneous NEAR membrane	93	<u>L1</u>

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L4: Entry 2 of 7

File: USPT

Sep 13, 1994

DOCUMENT-IDENTIFIER: US 5346924 A

TITLE: Heterogeneous ion exchange materials comprising polyethylene of linear low density or high density high molecular weight

Brief Summary Paragraph Right (1):

The invention relates to novel heterogeneous membranes, methods for producing such membranes, and apparatus employing such membranes.

Brief Summary Paragraph Right (4):

Current commercially available ion exchange membranes are primarily of two general types: homogeneous membranes and heterogeneous membranes. A homogeneous membrane is one in which the entire volume of the membrane (excluding any support material that may be used to improve strength) is made from the reactive polymer. Examples include membranes made of sulfonated or aminated styrene-divinylbenzene polymers (SDVB membranes), polymerized perfluorosulfonic acids (PFOS membranes) or various thermoplastics with active groups grafted onto the base polymer.

Brief Summary Paragraph Right (7):

In contrast, heterogeneous membranes are formed of 1) a composite containing an ion exchange resin to impart electrochemical properties and 2) a binder to impart physical strength and integrity. Typical heterogeneous membranes may be produced as "micro-heterogeneous" membranes by the paste method (in which ion exchange resin monomers are reacted to form the ultimate ion exchange resin polymer in the presence of a finely-ground inert binder polymer), or in the alternative, as "macro-heterogeneous" membranes by the physical blending of pre-polymerized ion exchange resin and binder.

Brief Summary Paragraph Right (8):

Present macro-heterogeneous membranes tend to have inferior electrochemical properties as compared to homogeneous or micro-heterogeneous membranes, but they do offer a number of advantages as compared to such membranes. In particular, macro-heterogeneous membranes are easy to manufacture and can be readily chemically modified since, within limits, the binder and resin types and content can be varied without significantly modifying the manufacturing process. Macro-heterogeneous membranes also tend to be stronger than homogeneous membranes, although they still generally require a screen or cloth support. Finally, macro-heterogeneous membranes can be dried without damage to the membrane.

Brief Summary Paragraph Right (9):

Unfortunately, present heterogeneous membranes are still difficult to manufacture. They typically are produced from a solvent-containing lacquer that is dangerous to handle and becomes hazardous waste. Furthermore, such membranes are often limited to the use of a binder that can be dissolved in a relatively non-toxic solvent. Finally, although not damaged upon drying, they do undergo substantial dimensional changes, thus making it difficult to fabricate them into devices in which drying may occur.

Brief Summary Paragraph Right (10):

The most common macro-heterogeneous membrane is a composite containing a styrene-divinylbenzene (SDVB) based resin, a polyvinylidene fluoride (PVDF) binder, and a polypropylene cloth support. The SDVB is usually mixed into a solution of PVDF dissolved in a solvent such as N-methyl pyrrolidone (NMP) to form a suspension. The suspension is coated onto the polypropylene support, dried in an oven and pressed in a heated press.

Brief Summary Paragraph Right (12):

The use of the polypropylene cloth, since it is not ionically conductive, has the

effect of further restricting the diffusion of ions through the membrane, thereby decreasing the electrochemical properties of the membrane as compared to competitive homogeneous membranes. Also, upon cutting the membrane to a desired size for a particular application, strands from the cloth tend to become exposed, and liquid within the membrane tends to diffuse to the membrane edges through the strands (a problem common to both homogeneous and heterogeneous membranes). This causes a liquid "weeping" or leaking phenomenon that detracts from the appearance and performance of devices such as plate and frame type equipment that have membrane edges exposed to the exterior of the device.

Brief Summary Paragraph Right (13):

An alternative way to manufacture heterogeneous ion exchange membranes using heat and pressure, as opposed to dissolution coating, described above is also well-known in the art. Such a method is usually used if the binder polymer is not readily dissolvable in a solvent. For example, U.S. Pat. Nos. 2,681,319 and 2,681,320 describe methods for producing heterogeneous membranes and methods for producing a film of controlled thickness. These references also describe post-conditioning of the membrane film using water.

Brief Summary Paragraph Right (15):

Subsequently, U.S. Pat. No. 3,876,565 sought to enhance the pliability of the heterogeneous membranes by expanding the ion exchange resins during conditioning. This was done by subjecting the membrane treatment in hot water at greater than 80.degree. C. Further improvements were described in U.S. Pat. No. 4,294,933 which sought to prevent micro-cracks, said to be produced during the formation process described in U.S. Pat. No. 3,876,565, by creating siloxane bridging linkages between the ion exchange resin and a vinyl-silane polyolefin copolymer binder. The reference also describes the use of lubricants in the formulation.

Detailed Description Paragraph Right (14):

In deionization applications, ion exchange membranes should have moderate to high ionic permselectivity (depending on whether low to high salinity water is fed to the membrane device, respectively), low water permeability, and low electrical resistivity. Tabulated below are typical values for membranes of different manufacturers as compared to the present invention. As can be seen in the tables, anion exchange membranes made in connection with the present invention have similar permselectivity and permeability to other commercially available membranes, lower to equal electrical resistivity as compared to other heterogeneous membranes depending on membrane thickness, and equal to greater electrical resistivity as compared to homogeneous membranes (depending on membrane thickness and ratio of ion exchange resin to LLDPE).

Detailed Description Paragraph Right (15):

Similarly, the cation exchange membranes made in accordance with the present invention have similar permselectivity to other membranes, lower to similar electrical resistivity as compared to other heterogeneous membranes, and equal to higher electrical resistivity as compared to the homogeneous membranes. Permeability is lower than the other membranes as well. Since permeability is a measure of micro-cracks, it can be seen that the invention has overcome the problem of micro-cracks reported in the prior art.

Detailed Description Paragraph Right (16):

Each of the commercial membranes described above requires a supporting cloth to have the physical strength to be fabricated into devices. In contrast, the present invention has the strength to function in a satisfactory manner without a supporting cloth or screen. Additionally, the absence of the cloth or screen support is the primary reason that LLDPE and HMWHDPE membranes can be produced having electrical resistivity comparable to the generally more conductive homogeneous membranes. The inventive membrane is dimensionally stable after conditioning, at which point it can be exposed to ambient environments with little or no shrinkage or damage. In contrast, other heterogeneous membranes shrink to a significant extent. Upon drying, homogeneous membranes crack and become damaged. The membrane of the present invention tends to lay flat after conditioning. The ability to lay flat is critical for maintaining close dimensional tolerances within membrane devices, and greatly simplifies device fabrication.

Detailed Description Paragraph Right (19):

In another aspect of the invention, the inventive membranes display enhanced fouling resistance over homogeneous membranes because the active surfaces of such homogeneous membranes are more exposed to slow diffusing foulants. Heterogeneous membranes tend to

be lower in fouling because they present a macrosurface of the binder material rather than the active resin. The membranes of the present invention display very little fouling because LLDPE and HMWHDPE binders exhibit hydrophobicity. This effect also allows the membrane to be more easily cleaned than conventional membranes.

Detailed Description Paragraph Right (23):

Bonding is extremely difficult with crosslinked homogeneous membranes because they are not heat weldable. Furthermore, although PVDF heterogeneous membranes are heat bondable to PVDF forms, since PVDF is extremely expensive as a general construction material, it makes heat bonding unattractive in most applications. To date, this difficulty with commercially available membranes has limited the designs of fabricated devices because commercially available membranes can either not be bonded (oftentimes causing the potential for device leaks), or must be bonded using adhesives. Adhesive bonding is a costly and difficult process that often limits temperature and chemical resistance. In addition, adhesive bonding may add extractables to the product liquid being treated.

Detailed Description Paragraph Type 1 (1):

PVDF 1=Ionpure supported heterogeneous membrane with PVDF binder.

Detailed Description Paragraph Type 1 (2):

MA-3475, MC-3470=Sybron supported heterogeneous membrane with PVDF binder.

Detailed Description Paragraph Type 1 (3):

AMI-7001, CMI-7000=Membrane International supported heterogeneous membrane with PVDF binder.

Detailed Description Paragraph Type 1 (4):

PVDF 2=Hydro supported heterogeneous membrane with PVDF binder.

CLAIMS:

11. A membrane which comprises the heterogeneous ion exchange material of claim 1 .

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L4: Entry 4 of 7

File: USPT

Sep 3, 1991

DOCUMENT-IDENTIFIER: US 5045171 A

TITLE: Acid efficient membrane for use in electrodialysis for recovery of acid

Brief Summary Paragraph Right (25):

According to a second method, a powdered thermoplastic film-forming polymer (such as the homo- or co-polymers of vinyl chloride, vinyl fluoride, vinylidene chloride, vinylidene fluoride, ethylene and propylene or polymers such as styrene-butadiene copolymer, hydrogenated styrenebutadiene block copolymer, butyl rubber, chlorinated butyl rubber, poly chloroprene, sulfochlorinated polyethylene or acrylonitrile-styrenebutadiene terpolymer) is dissolved in the mixture of functional monomer, polymerization initiator and/or photosensitizer, crosslinking monomer and leachable diluent. (The latter is frequently a dialkyl phthalate). A suitable fabric is impregnated with such resulting paste, or organosol and the impregnated fabric processed as outlined in the description of the first method. Alternatively a film (including a fabric reinforced film) of the above mentioned film forming polymer is impregnated with the mixture of monomers, diluent and initiator and/or photosensitizer, the impregnated film then further processed as outlined above.

Brief Summary Paragraph Right (29):

A fourth method for making commercial anion selective membranes known in the prior art entails kneading or milling pulverized anion exchange resin into a film forming thermoplastic (including thermoplastic elastomers such as SBS or SIS block copolymers), calendering such mixture onto a suitable fabric or extruding the mixture into a sheet and subsequently bonding one or more such sheets to one or more fabrics. Commercially available granular anion exchange resins have water contents substantially in excess of about 5 mols per-equivalent of anion exchange capacity (see for example Table 16-4, "Perry's Chemical Engineer Handbook, 6th Edition" McGraw-Hill) NY, (1984)). Such heterogeneous membranes are made by Ionac Chem. Div., U.S.A.

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L4: Entry 1 of 7

File: USPT

Apr 30, 2002

US-PAT-NO: 6379796

DOCUMENT-IDENTIFIER: US 6379796 B1

TITLE: Composite hollow fiber membrane

DATE-ISSUED: April 30, 2002

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Uenishi; Masamoto	Otake			JPX
Fukushima; Noriaki	Otake			JPX

US-CL-CURRENT: 428/398; 428/375, 428/397

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments	Claims	KWIC
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☐ 2. Document ID: US 5346924 A

L4: Entry 2 of 7

File: USPT

Sep 13, 1994

US-PAT-NO: 5346924

DOCUMENT-IDENTIFIER: US 5346924 A

TITLE: Heterogeneous ion exchange materials comprising polyethylene of linear low density or high density high molecular weight

DATE-ISSUED: September 13, 1994

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Giuffrida; Anthony	North Andover	MA		

US-CL-CURRENT: 521/28; 204/296, 204/632, 210/263, 210/321.6, 210/500.23, 210/500.36, 264/122, 264/126, 428/364, 428/372, 428/500, 428/516, 428/521, 521/27, 521/29

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments	Claims	KWIC
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☐ 3. Document ID: US 5238613 A

L4: Entry 3 of 7

File: USPT

Aug 24, 1993

US-PAT-NO: 5238613
DOCUMENT-IDENTIFIER: US 5238613 A

TITLE: Microporous materials

DATE-ISSUED: August 24, 1993

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Anderson; David M.	Buffalo	NY	14114	

US-CL-CURRENT: 264/425; 210/500.27, 210/500.35

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments	KWC
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☒ 4. Document ID: US 5045171 A

L4: Entry 4 of 7

File: USPT

Sep 3, 1991

US-PAT-NO: 5045171
DOCUMENT-IDENTIFIER: US 5045171 A

TITLE: Acid efficient membrane for use in electrodialysis for recovery of acid

DATE-ISSUED: September 3, 1991

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
MacDonald; Russell J.	Watertown	MA		

US-CL-CURRENT: 204/630; 204/252, 204/296, 204/633, 521/27

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments	KWC
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☐ 5. Document ID: US 5035791 A

L4: Entry 5 of 7

File: USPT

Jul 30, 1991

US-PAT-NO: 5035791
DOCUMENT-IDENTIFIER: US 5035791 A

TITLE: Ion sensor containing a selective organic membrane

DATE-ISSUED: July 30, 1991

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Battilotti; Massimo	Rome			ITX
Giongo; Matteo	Rome			ITX

US-CL-CURRENT: 204/415; 204/416, 204/418, 257/253

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
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KWC

☐ 6. Document ID: US 4909971 A

L4: Entry 6 of 7

File: USPT

Mar 20, 1990

US-PAT-NO: 4909971

DOCUMENT-IDENTIFIER: US 4909971 A

TITLE: Process for making a heterogeneous membrane film

DATE-ISSUED: March 20, 1990

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Coughlin; Michael C.	Kingston			CAX
Moss; Arthur Z.	Wilmington	DE		
Stevens; Kenneth E.	Kingston			CAX

US-CL-CURRENT: 264/45.5; 264/210.6, 264/288.8, 264/45.3, 264/45.9, 264/46.1

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
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KWC

☐ 7. Document ID: US 4842741 A

L4: Entry 7 of 7

File: USPT

Jun 27, 1989

US-PAT-NO: 4842741

DOCUMENT-IDENTIFIER: US 4842741 A

TITLE: Heterogeneous membranes from highly filled thermoplastic orientable polymers

DATE-ISSUED: June 27, 1989

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Coughlin; Michael C.	Wilmington	DE		
Moss; Arthur Z.	Wilmington	DE		
Stevens; Kenneth E.	Kingston			CAX

US-CL-CURRENT: 210/500.36; 210/490, 264/288.8, 264/41

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
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(((L1) AND (L2 SAME L3))).USPT.	7

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